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PATENT SPECIFICATION

(11) 1 525 978

1 525 978

- (21) Application No. 51470/75 (22) Filed 16 Dec. 1975
- (31) Convention Application Nos. 533 019, 533 020 and 533 021
- (32) Filed 16 Dec. 1974 in
- (33) United States of America (US)
- (44) Complete Specification published 27 Sept. 1978
- (51) INT CL² C08F 2/34//10/02, 10/06
- (52) Index at acceptance C3P LA



(54) POLYMERIZATION PROCESS AND APPARATUS

PATENTS ACT 1949

SPECIFICATION NO 1525978

The following corrections were allowed under Section 76 on 11 October 1978:

Page 2, line 77, *after between delete compartments insert zones*

Page 2, line 79, *after one delete compartment insert zone*

THE PATENT OFFICE
13 November 1978

Bas 51407/12

- 20 process can be considerably more economical
if certain problems inherent in vapor state
polymerization can be solved. These include
problems of carrying out the polymerization in
a thermally controlled fashion so as to avoid
25 hot spots, maintaining a proper product par-
ticle size distribution and, in the case where
catalysts are utilized which have extremely
high yields but are extremely sensitive to
poisoning, decreasing to a minimum the
30 amount of make-up material seen by the cata-
lyst per amount of product formed. Another
problem related to certain catalyst combina-
tions is the narrow molecular weight distribu-
tion of the products formed with these cata-
35 lysts. Now we have developed a vapor phase
reactor which largely or completely solves the
above referred to problems and reaps important
economic benefits through savings in energy
consumption, raw materials and capital costs.
- 40 According to one aspect of the present in-
vention, there is provided a continuous process
for vapor phase polymerization of at least one
polymerizable monomer, which process com-
prises polymerizing said monomer in the vapor
45 phase, in a horizontal polymerization zone
and in the presence of catalyst and a stirred
subfluidized (as defined herein) particulate
polymer bed in said zone; spraying a readily
horizontal polymerization zone therein; a cen-
trally located rotatable shaft extending longi-
tudinally through the reactor to which are
70 attached a plurality of adjacently located and
circularly offset flat impellers; drive means
for rotating said shaft, one or more inlets
spaced along the bottomward part of the reac-
tor for introducing feed-gas comprising mono-
75 mer vapor to said polymerization zone; one or
more inlets for introducing catalyst to said
polymerization zone; one or more inlets spaced
along the topward part of the reactor for in-
80 troducing quench liquid to said polymeriza-
tion zone; one or more outlets spaced along
the topward part of the reactor for removing
off-gases from said polymerization zone; and
means for removing polymer product from the
85 reactor.
- Preferably the reactor utilizes a controlled
introduction of catalyst components and
quench liquid into two or more polymerization
sections directly onto and into the stirred, sub-
90 fluidized bed of forming polymer and poly-
merization of monomer from the vapor phase
in and over such bed. The polymer solid may
be continuously removed by passing through a
take-off divider generally at one end of the
95 reactor into a take-off vessel. The reactor intro-
duces monomer or a mixture thereof and,

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(54) POLYMERIZATION PROCESS AND APPARATUS

(71) We, STANDARD OIL COMPANY, a corporation organized and existing under the laws of the State of Indiana, U.S.A., of 200 East Randolph Drive, Chicago, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel apparatus and process for the vapor state polymerization of a polymerizable monomer or mixture thereof to produce normally solid polymeric substances.

One of the problems in solution or slurry polymerization of monomers is the capital costs required in the production thereof. Monomer polymerization using a vapor phase process can be considerably more economical if certain problems inherent in vapor state polymerization can be solved. These include problems of carrying out the polymerization in a thermally controlled fashion so as to avoid hot spots, maintaining a proper product particle size distribution and, in the case where catalysts are utilized which have extremely high yields but are extremely sensitive to poisoning, decreasing to a minimum the amount of make-up material seen by the catalyst per amount of product formed. Another problem related to certain catalyst combinations is the narrow molecular weight distribution of the products formed with these catalysts. Now we have developed a vapor phase reactor which largely or completely solves the above referred to problems and reaps important economic benefits through savings in energy consumption, raw materials and capital costs.

According to one aspect of the present invention, there is provided a continuous process for vapor phase polymerization of at least one polymerizable monomer, which process comprises polymerizing said monomer in the vapor phase, in a horizontal polymerization zone and in the presence of catalyst and a stirred subfluidized (as defined herein) particulate polymer bed in said zone; spraying a readily

vaporizable quench liquid onto the surface of said stirred particulate polymer bed to control the polymerization temperature by evaporative cooling in said polymerization zone; removing off-gases comprising monomer vapor and quench liquid vapor from said polymerization zone to form an off-gas stream; and recovering particulate polymer from said polymerization zone.

As used herein to describe a stirred particulate polymer bed, the term "subfluidized" is intended to indicate that the polymer particles in the bed are not suspended in gases introduced beneath the bed.

The invention also provides a polymerization reactor for carrying out the polymerization process described above, comprising a generally cylindrical reaction vessel arranged with its axis horizontal so as to provide at least one horizontal polymerization zone therein; a centrally located rotatable shaft extending longitudinally through the reactor to which are attached a plurality of adjacently located and circularly offset flat impellers; drive means for rotating said shaft, one or more inlets spaced along the bottomward part of the reactor for introducing feed-gas comprising monomer vapor to said polymerization zone; one or more inlets for introducing catalyst to said polymerization zone; one or more inlets spaced along the topward part of the reactor for introducing quench liquid to said polymerization zone; one or more outlets spaced along the topward part of the reactor for removing off-gases from said polymerization zone; and means for removing polymer product from the reactor.

Preferably the reactor utilizes a controlled introduction of catalyst components and quench liquid into two or more polymerization sections directly onto and into the stirred, subfluidized bed of forming polymer and polymerization of monomer from the vapor phase in and over such bed. The polymer solid may be continuously removed by passing through a take-off divider generally at one end of the reactor into a take-off vessel. The reactor introduces monomer or a mixture thereof and,

optionally, hydrogen largely or wholly under-
neath the polymer bed and quench liquid onto
the surface of the bed. The reactor polymeriza-
tion zone or zones preferably have two or
5 more polymerization sections and the several
sections are separated from each other by
weirs to prevent gross back-mixing between
sections. Each section may be individually
10 controlled in terms of polymerization tempera-
ture and polymer production rate so that a
polymeric product having a controlled spread
of molecular weight and particle size may more
easily be produced.

Reactor off-gases are removed along the
15 top of the reactor after removing entrained
polymer fines as completely as possible from
the off-gases. The reactor off-gases are then
taken to a separation zone whereby the quench
20 liquid is at least in part separated along with
any further polymer fines and some of the
catalyst components from gaseous monomer
and hydrogen, if used, which monomer and
hydrogen are then recycled to inlets spaced
25 along the various polymerization sections of
the reactor and located largely or wholly
underneath the surface of the polymer bed. A
portion of the quench liquid including the fur-
ther polymer fines is taken off the separation
30 zone and in major part returned to inlets
spaced along the top of the reactor. A minor
part of such quench liquid purified of poly-
mer fines and catalyst components is fed into
a catalyst make-up zone for catalyst diluent
35 so that fresh quench liquid need not be intro-
duced for that purpose. Provision may be
made in the multiple section reactor to intro-
duce the catalyst components and quench
liquid at different rates into the different sec-
40 tions of the reactor to aid in individual con-
trol of the polymerization temperatures and
polymer production rates of the various sec-
tions. Catalyst components may be added into
or onto the stirred bed.

The reactor is particularly adapted for use
45 with polymerization catalysts which have a
high enough polymerization yield that catalyst
residues need not be removed from the poly-
meric product during the polymer finishing
process. In general, the reactor utilizes a con-
50 trolled introduction of catalysts and quench
liquid into the one or more polymerization
sections contained in each zone directly into
and onto the stirred, subfluidized bed of form-
ing polymer solid and polymerization of mono-
55 mer from the vapor phase in and over such
bed. The polymer solid is continuously re-
moved by passing through a take-off divider
generally situated at one end of the reactor
into a take-off vessel.

60 The reactor introduces monomer or a mix-
ture thereof and, optionally, hydrogen largely
or wholly underneath the polymer bed and
quench liquid onto the surface of the bed.
Each polymerization zone has a separate off-
65 gas removal line, a quench liquid separation

zone and a separate vapor recycle return. Each
zone of the reactor may have one or more
polymerization sections separated by weirs to
prevent gross backmixing between sections.
Each section may be individually controlled
in terms of polymerization temperature and
polymer production rate.

The reactor may be divided into two or
more polymerization zones separated by a
divider filling the cross-sectional area of the
reactor and so constructed that it serves to con-
75 trol vapor intermixing between compartments
but allows free polymer particle movement
from one compartment to the other essentially
in the direction of the take-off. A polymeric
product having a controlled spread of molec-
80 ular weight, molecular weight distribution
and particle size distribution is more easily
produced by the above described reactor.

Reactor off-gases from each zone are re-
85 moved along the top of the reactor after re-
moving polymer fines as completely as possible
from the off-gas stream. Such reactor off-
gases are led to a separation zone whereby the
quench liquid is at least in part separated
90 along with any further polymer fines and some
of the catalyst components from polymerization
monomer and hydrogen, if used, which mono-
mer and hydrogen, are then recycled to inlets
spaced along the various polymerization sec-
95 tions of the polymerization zone generally un-
derneath the surface of the polymer bed. A
portion of the quench liquid including the fur-
ther polymer fines is taken off the separation
zone and in major part returned to inlets
100 spaced along the top of the reactor. A second
small portion of separated quench liquid free
of polymer fines and catalyst components is
fed into a catalyst make-up zone for catalyst
diluent so that fresh quench liquid need not
105 be introduced for that purpose. Provision may
be made to introduce the catalyst components
and quench liquid at different rates into one or
more of the polymerization sections of each of
the polymerization zones to aid in control of
110 the polymerization temperatures and polymer
production rates. Catalyst components may
be added on the surface or below the surface
of the bed.

By the term vapor phase reactor or process
115 is meant a reactor or process, the monomer or
monomers of which are vapors or gases under
the conditions prevailing in the reactor.

The recycle system and reactor are prefer-
ably so designed that they operate essentially
120 isobarically. That is no more than the normal
operation variations are present. Preferably,
the reactor and recycle system pressure varia-
tions are no more than ± 25 psig and, more
preferably, no more than ± 10 psig.

Apparatus according to the invention will
now be described by way of example with par-
ticular reference to the accompanying drawings
of which:

Figure 1 shows a longitudinal view of one 130

embodiment of the reactor described herein.

Figure 2 shows a transverse view of such reactor along line 2—2 of Figure 1.

Figure 3 shows a second transverse view of the reactor of Figure 1 along line 3—3 of Figure 1.

Figure 4 shows one embodiment of an essentially isobaric process by which the reactor described herein is employed with essentially total reactor off-gas recycle.

As may be seen by looking at Figure 4, which Figure may be divided roughly into two areas, the reactor area and the reactor off-gas treatment (separation) and catalyst make-up area, the polymerization zone of horizontal polymerization reactor 401 is divided into several stirringly agitated sections 467, 469, 471 and 473 to provide for the possibility of operating the different sections of the polymerization zone at different temperatures and/or different polymer production rates. Polymerization takes place in each of the aforementioned sections to form a polymer bed the polymerization zone of the reactor and the polymerization temperature of each of the sections may be individually controlled by a combination of methods including the stirring agitation, the controlled differential introduction of vapor recycle into each of the sections through inlets 475, 477, 479 and 481 spaced along the bottom of the reactor, and the introduction into each of the sections of inert quench liquid and catalyst components at different rates through quench liquid inlets 453, 455, 457 and 459 and catalyst inlets 423, 425, 427 and 429 spaced along the top of the reactor.

Reactor off-gases are removed through outlets 483, 485, 487, and 489. Since a certain deleterious amount of polymer fines may be produced in the reactor they advantageously are substantially removed prior to transfer of the reactor off-gases to the reactor off-gas treatment and catalyst make-up area using traps, filters, settlers, cyclones or scrubbers or a combination thereof.

Polymer solid is produced in each of the stirringly agitated sections 467 through 473 and, due to the continued production of such polymer, an amount of product constantly passes through the take-off divider and out of the reactor into polymer take-off vessel 403.

Catalyst, dissolved or slurried in recycle quench liquid, is advantageously introduced onto the surface of the bed in at least one of the various polymerization reaction sections through inlets 423, 425, 427 and 429. Similarly placed inlets 453, 455, 457, and 459 are used to introduce the recycle quench liquid, which may contain cocatalyst, onto the bed in the individual reaction sections. However, depending on the nature of the catalyst, cocatalyst and monomer to be polymerized, catalyst and/or cocatalyst can be sprayed or otherwise introduced into the reactor neat or in other

non-polymerizable vehicles. Alternatively, for some monomers, catalyst and cocatalyst can be added to make-up zone 445 and together added to reactor 401.

In one mode of operation it has been found advantageous to make the catalyst and quench liquid inlets concentric so that the catalyst and quench liquid are sprayed into the reactor and onto the surface of the polymer bed in such a way as to more evenly distribute the catalysts on the polymer bed surface. However, the catalyst and quench inlets may be made separate and the catalysts and quench liquid introduced separately onto the bed.

The reactor off-gases are taken via line 431 to scrubber tower 433 wherein at least part of the quench liquid component of the off-gases, further polymer fines and some of catalyst components are removed from the polymerizable monomer vapor and hydrogen, if used. The polymerizable monomer and hydrogen together with some quench liquid vapor are returned to reactor 401 from the top of scrubber tower 433, after, advantageously, passing through heat exchanger 460 and separator 461 to condense out additional quench liquid, via blower 444 and vapor recycle line 456 with additional hydrogen and gaseous monomer make-up being added via lines 463 and 465. Alternatively, monomer and hydrogen can be returned from scrubber tower 433 to reactor 401 bypassing heat exchanger 460 and separator 461. The amount of vapor recycle introduced into the individual sections of the reactor via inlets 475, 477, and 481 can be individually controlled by valves 491, 493, 495, and 497 and the bed thereby kept in a subfluidized state. The quench liquid of separator 461 is essentially free of polymer fines and catalyst components and suitable for use in catalyst make-up zone 445.

Quench liquid, separated from the reactor off-gases, is cooled by heat exchanger 454 and returned in major portion to the top of scrubber tower 433 via line 438. A minor portion of the quench liquid is returned through line 437, heat exchanger 443, pump 439 and quench liquid recycle line 451 to quench liquid inlets 453, 455, 457, and 459 carrying with it some monomer, hydrogen, cocatalyst and any polymer fines carried by the off-gases into scrubber tower 433. Quench liquid make-up may be added via line 440. In the important embodiment in which cocatalyst is used, make-up cocatalyst may be added to catalyst make-up zone 445, injected directly into the recycle quench liquid stream through line 447 or may be added directly in a non-polymerizable vehicle into reactor 401. A small portion of quench liquid essentially free of polymer fines and catalyst components is taken off separator 461 and passed through line 434 and pump 436 to catalyst make-up zone 445 for catalyst make-up purposes.

Polymerization in catalyst make-up zone

445 or associated line 449 and inlets 423—429 can cause serious plugging problems and may be controlled by keeping the cocatalyst concentration in catalyst make-up zone 445 below a certain value, which value depends upon the identity of the catalyst and cocatalyst used and the monomer to be polymerized. Where make-up cocatalyst is added to catalyst make-up zone 445 provision may have to be made to prevent polymerization from occurring in associated lines by cooling the make-up zone or decreasing the residence time of the catalyst components therein. Alternatively, make-up quench liquid from line 447 can be used in catalyst make-up zone 445 in place of recycle quench liquid to prevent polymerization of monomer in said zone.

Valve 499 has been provided in the catalyst make-up zone bypass line in order to more easily vary the concentration of catalyst in the catalyst make-up introduced into the reactor. It has been found that the particle size of the polymer produced in reactor 401 can be advantageously varied by varying the concentration of the catalyst being introduced through inlets 423, 425, 427 and 429. Further, it has been found advantageous to vary the catalyst concentration either by changing its concentration in make-up zone 445 or, additionally and alternatively, to change its concentration by introducing quench liquid into catalyst line 449 via valve 499 just prior to the point where the catalyst enters the catalyst inlets 423, 425, 427, and 429. Make-up catalyst is added through line 442.

The particulate solids which build up in stirred reactor 401 traverse the length of reactor essentially because of polymer build-up in the reactor bed and not by the stirring agitation. This condition is insured by the impeller design used which provides for agitation but not for backward or forward movement of the bed. Polymer particles in the bed adjacent to the take-off divider are swept by the stirring through the take-off divider opening, which opening may be made variable in size and position by a number of devices for maintaining different levels of polymer solid in the reactor.

Weirs, if used, may be attached to drive shaft 404 with slip rings or fixed to the walls of the reactor and are beneficially oriented so that the top of the weir is roughly aligned with the bed orientation during agitation. This provides for spill-over along the entire length of the weir top. However, the weirs can be oriented horizontally, if desired. Other means may be used in place of the weirs to prevent gross back-mixing between the two or more sections of the reactor. For example, thin wall dividers attached to drive shaft 404 which fill the reactor cross-section and have one or more holes cut in them may be used as can be understood by one skilled in the art.

The polymer particles passing through such

take-off divider opening fall into polymer take-off vessel 403. The polymer solid taken off can be treated with additives and melt extruded in the ways conventional to the art or it can be taken off without substantial pressure letdown in such a way that the solid is melted in vessel 403 and the resulting molten polymer treated with kill substance (catalyst deactivators) and additives and devolatilized while still in the molten state and then finished into commercially sized product by conventional techniques.

Figure 1 shows in detail reactor 401 of Figure 4 and which is referred to as reactor 101 in Figure 1. It may be seen that the interior of reactor 101 is composed of four individually controllable polymerization sections 167 to 173 separated from one another by weirs 110 to 114, which weirs extend upwardly to somewhat over the middle of the reactor and are oriented so that their top surfaces line up approximately with the polymer bed surface during agitation. In a favoured embodiment weirs 110, 112 and 114 are constructed in height so that the polymer bed fills about half the volume of the reactor. As the solid polymer exceeds the weir height it falls into the adjacent section moving in the direction of the take-off.

In a mode wherein it is desired to operate with two or more gas compositions (different hydrogen concentrations) as well as different section temperatures, all the weirs are constructed as above except for one or more thin wall dividers which divide the reactor into polymerization zones having different gas compositions. The thin wall dividers fill the cross-section of the reactor and contain an opening situated beneath the level of the polymer bed for polymer solid movement. Gas intermixing between the zones is thereby controlled. Operating in such a variable gas composition mode, the individual zones should have separate reactor off-gas recycle treatments and returns and may have separate hydrogen and monomer make-ups.

Generally, the dividers are designed to prevent extensive intermixing of the vapors between the individual compartments, however in one mode of multiple hydrogen operation the vapors are deliberately mixed by feeding the vapors from the hydrogen poor zone to the hydrogen rich zone and adding make-up monomer primarily to the hydrogen poor zone and hydrogen make-up primarily to the hydrogen rich zone.

The interior of the reactor is equipped with a rotating impeller drive shaft 104 extending longitudinally through reactor 101 to which are attached impellers extending transversely from the shaft and making close clearance with the inside wall of reactor 101 to insure adequate bed mixing at the reactor wall. The impellers are preferably flat to maximise bed agitation for a given rotational speed. The

width of the impellers is such that between four and twelve impellers will be present in a reactor section of about three feet in length. The orientation of the adjacent impellers is about ninety degrees. The impellers are so constructed to minimize any forward or backward movement of the bed during stirring and are driven by motor 102 at such a speed as to give a slow and regular turnover of the entire polymer bed contained in the reactor. The speed at which the impellers turn should be fast enough to provide the desired heat and mass transfer between liquid, solid and gas but not so fast that the finer portions of the polymer bed are thrown up in large quantities into the space above the bed. That is, the speed typically is five to thirty RPM so that the integrity of the bed is maintained.

The space following the take-off divider and above the take-off vessel is likewise equipped with one or more similar impellers, 120, the number of which depend upon the size of the take-off. However, take-off assemblies such as end or side take-off apertures, which assemblies replace the take-off divider may be used as can be understood by one skilled in the art.

A plurality of catalyst and quench inlets can be used in reactor 101 and one or more pairs of catalyst and quench inlets may be used for each reactor section, 167 to 173. The catalyst and quench inlets are typically designed so that the catalyst and quench liquid are distributed onto the top of the agitated bed at roughly the same location. Such introduction of catalyst and quench liquid combined with slow agitation has been found to provide more uniform polymerization and prevent localized fusion in the polymer bed and hence reduce the number of molten plugs of polymer formed and give more trouble free performance of the reactor. It is advantageous in one mode of carrying out polymerization in the reactor to provide for separately controlled addition of catalyst components and quench liquid into the various sections by means of, for example, valves. Such separately controlled additions into reactor sections 167 to 173 help provide for separate control of polymerization temperatures and polymer production rate among the sections and can be used to vary and control the molecular weight and particle size distribution of the polymer.

The vapor which includes fresh and recycle gaseous polymerizable monomer or monomers and hydrogen, if used, is brought in through monomer vapor feed line 156 to vapor inlets 175 to 181 at a rate designed to prevent fluidization of the bed. The rate at which the gases are introduced into the individual sections 167 to 173 can be controlled by valves 191 to 197 and such control may be used to help vary the section polymerization temperatures and polymer production rates if desired.

In an important embodiment of the process using the reactor described herein in which

the polymerization temperature of one or more of the sections is held at a different value than in the other section or sections (dual temperature operation or multi-temperature operation), it is advantageous to vary the concentrations of any or all of the catalyst components being introduced into the various sections. Particle size distribution and molecular weight distribution are advantageously affected thereby. This may be accomplished by feeding the catalyst inlets of the different sections individually. Even in single temperature operation, it can be advantageous to feed one or more of the sections with catalyst components at different concentrations than catalyst components being introduced into the other section or sections.

The overall reactor temperature range for polymerization depends upon the particular monomer which is being polymerized and the commercial product desired therefrom and as such are well known to those skilled in this art. In general, the temperature range used varies between 40°C up to the softening temperature of the bed. The total polymerization pressure is composed of the polymerizable monomer pressure, vaporized quench liquid pressure and hydrogen pressure, if used. The individual partial pressures of the components making up the total pressure determine the rate at which polymerization occurs, the molecular weight, and the molecular weight distribution of the polymer to be produced. The temperature of polymerization is controlled as may be understood by one skilled in the art.

False end plates inserted in reactor 101 for mechanical construction purposes are shown as 124 and 126.

In Figure 2 a view of reactor 101 of Figure 1 is shown along line 2—2 of Figure 1. The Figure shows the ninety degree orientation of adjacent impellers, the adjustable take-off divider opening 218 and take-off divider 216. Further, the Figure shows the orientation of weir 214 and the polymer bed in reactor 201 and the direction of paddle movement with respect to the bed orientation.

Figure 3 shows a view of reactor 101 to Figure 1 along line 3—3 of Figure 1. Also shown are take-off divider 316, its opening 318 and the direction of motion of the impellers with respect to take-off divider opening 318 and the orientation of the polymer bed.

The apparatus and process described herein may be applied to the polymerization of polymerizable monomers which are polymerizable below the softening point of their polymeric forms including ethene, propene, 4-methyl-pentene-1, butene-1, vinyl chloride, butadienes, styrene and mixtures of such monomers. Particularly suitable are the polymerization of ethene and propene.

The quench liquid used for temperature control is a readily volatilizable liquid which can be sprayed onto the surface of the polymer

bed to evaporatively conduct heat away from the polymer bed and maybe the monomer itself in liquefied form or some other liquid which is inert to the monomer being polymerized, the catalyst components used in the polymerization, and have as high a heat of evaporation as is consistent with ready volatilization of the quench liquid in the reactor at the polymerization temperature. In general alkanes such as propane, a butane, a pentane, or a hexane or closely boiling mixtures thereof may be used. The preferred quench liquid for ethene is isobutane or isopentane. It should be understood that where the monomer to be polymerized is readily condensable, e.g. propene, the quench liquid can be liquified monomer or a mixture of liquified monomer and an additional quench liquid.

The rate of quench liquid addition should be low enough to keep the polymer bed dry, i.e. maintain the partial pressure of the quench liquid vapor below the dew point, yet large enough to obtain the maximum cooling effect of the quench liquid. Generally, the quench liquid will carry away fifty percent or more of the heat of polymerization. For propene polymerization over ninety percent of the heat of polymerization is desirably removed by the quench liquid. at a 200°F polymerization temperature in the polymerization of ethene, desirably more than seventy percent of the heat of polymerization is removed using isobutane and more than fifty percent of the heat is removed using isopentane.

In general, the catalysts which are most useful to the process described herein are those which are very active and give a high yield on catalyst. Included in this group are cocatalysts composed of organometallic compounds of Periodic Group IA, IIA and IIIA and catalysts which are based on transition metal compounds. Aluminum alkyl compound cocatalysts are especially preferred and may be a trialkylaluminum or an alkyl aluminum halide such as a dialkylaluminum chloride. The transition metal catalyst can be a metal compound of Group IV or Group V such as a titanium or vanadium compound, a compound of Group VI such as chromium or molybdenum oxide or may be one of the above catalysts supported on a magnesium-based support or a support such as alumina, silica, or silica-alumina.

The preferred catalysts and cocatalysts are as aforesaid high yield catalysts. By high yield is meant catalysts and cocatalysts the residues of which do not have to be removed from the products of the process.

The preferred catalysts and cocatalysts for ethene polymerization are a trialkylaluminum cocatalyst with a catalyst which is a titanium compound supported on magnesium based sup-

port or chromium oxide supported on alumina, silica or combinations thereof. For propene polymerization it is preferable to use a dialkylaluminum chloride cocatalyst and a catalyst which is an active titanium trichloride. However, the process and apparatus described herein are not meant to be limited to the catalyst and cocatalyst used except in that the apparatus and process operate best using high yield catalysts.

The process of the invention is described in more detail in the specific Examples below. The reactors used were of the general type illustrated in Figure 1.

EXAMPLE I.

A supported titanium chloride catalyst was suspended in isopentane at a concentration of 30 milligrams/liter and pumped continuously to the reactor at a rate of 300 milliliters/hour. Aluminum triethyl diluted with isopentane to 1000 milligrams/liter was pumped continuously at a rate to maintain the desired weight ratio of aluminum triethyl/catalyst, 3/1 to 15/1. Ethene was charged continuously at the rate of polymerization to maintain pressure, 300 psig. A continuous stream of gas, 0.3 cubic feet/hour, was removed from the reactor for gas chromatographic analysis to maintain the hydrogen concentration in the reactor at 34 mol percent by intermittent hydrogen addition for polymer molecular weight control. The reactor polymer bed temperature was held at 160°F. by continuously spraying isopentane at the appropriate rate onto the 30 R.P.M. stirred polymer bed. The vaporized isopentane was condensed and recycled. The non-condensed gas (40 to 50°F.) was continuously recycled back into the bottom of the stirred polymer bed. The polymer bed level was maintained by the opening position in the take-off divider. The polymer overflow spilled out into the melter which was maintained at 350 to 400°F. by a combination of polymerization heat and external electrical heat. The melted polymer sumped to the bottom and was forced through a horizontal piece of $\frac{3}{4}$ inch diameter \times 4 foot long pipe at 400 to 500°F. by the reactor pressure. Water was injected continuously into the polymer melt between the melter and catalyst deactivator at a rate of 10 milliliters/hour. Polymer melt extruded from the catalyst deactivator through a $\frac{3}{8}$ inch diameter opening and is drawn through a water bath and chopped. Polymer was produced at the rate of 1 to 3 pounds/hour at a yield level of 100,000 grams polymer/gram catalyst. Physical properties of the polymer taken out of the melter are shown below in Table I and some properties of the polymer powder taken from the reactor are shown in Table II.

TABLE I

Conditions: 160°F, 300 psig, 34 mol percent H₂, 13/1 to 15/1 triethyl aluminum/catalyst weight ratio

| General Properties | Run A | Run B ⁽¹⁾ |
|--|---------|----------------------|
| Unannealed density, grams/cubic centimeter | 0.961 | 0.959 |
| Annealed density, grams/cubic centimeter | 0.977 | 0.977 |
| Inherent viscosity, dl/gram | 1.87 | 2.29 |
| Melt index, MF ₁ , grams/10 minutes | 0.92 | 0.44 |
| Melt index, MF ₁₀ , grams/10 minutes | 38 | 24 |
| Flow rate ratio, MF ₁₀ /MF ₁ | 41.4 | 54.5 |
| Hexane extractables, weight percent | 0.47 | 0.41 |
| Oven volatiles content, weight percent | 0.20 | 0.28 |
| Stiffness, psig | 165,500 | 160,000 |
| Molecular Weight Parameters, GPC | | |
| Molecular weight distribution, $\overline{M}_w/\overline{M}_n$ | 7.6 | 10.5 |
| Tensile Properties | | |
| Tensile strength at yield, psig at 2 inches/minute | 4540 | 4600 |
| Tensile strength at ultimate, psig at 2 inches/minute | 3410 | 2810 |
| Elongation at yield, percent at 2 inches/minute | 10 | 11 |
| Elongation at ultimate, percent at 2 inches/minute | 1200 | 689 |
| Impact Properties | | |
| Tensile impact strength, ft-lb/in ² | 65 | 88 |
| Izod impact strength, ft-lb/in notch | 9.2 | 9.8 |
| Thermal Properties | | |
| Vicat softening point, °F. | 266 | 262 |
| Brittleness temperature, °C. | — | — |

⁽¹⁾ Triethylaluminum/catalyst weight ratio = 2.6/1 to 3.75/1.

TABLE II

Conditions: 160°F., 300 psig, 34 mol percent H₂, 13/1 to 15/1 triethylaluminum/catalyst weight ratio.

| Cut number | Run A | | | Run B |
|--------------------------------------|-------|------|------|-------|
| | 5R | 8R | 10R | |
| Total polymer produced, grams | 3628 | 5509 | 6637 | 1952 |
| Inventory turnover (No. of times) | 3.0 | 4.6 | 5.5 | 1.5 |
| Percent original inventory remaining | 5 | 1 | 0.4 | 20 |
| Bulk density, grams/cubic centimeter | 0.36 | 0.37 | 0.37 | 0.41 |
| Mf ₁₀ | 28.7 | 38.7 | 48.2 | |
| MF ₁ | 0.89 | 1.0 | 1.3 | |
| MF ₁₀ /MF ₁ | 32.3 | 38.7 | 37.1 | |

EXAMPLE II.

A carbon steel reactor approximately 2 feet in diameter by 3.0 feet in length was used in this continuous ethene-propene polymerization. Temperatures were 181°F at one end of the reactor, 171°F at the center of the reactor and 181°F near the take-off divider end and reactor total pressure was 400 psig. Ethylene was fed to the reactor at 20.57 pounds/hour and propylene was added at 0.29 pounds per hour. The recycle gas rate was 2.29 actual cubic feet per minute and the recycle quench liquid, isopentane, rate was 0.29 gallons/minute. The supported titanium catalyst was added at about 0.3 grams per hour as a dilute slurry in isopentane. The amount of slurry added was about 3 gallons per hour. Triethylaluminum cocatalyst was added as a solution in isopentane at a rate of 35 milliliters per hour at a concentration of 0.025 grams triethylaluminum per milliliter.

Gas analyses of reactor recycle gases were continuously made and typical values were:

hydrogen, 37 mol percent; ethane, 0.3 mol percent; propene, 1.1 mol percent; isopentane, 1 mol percent and ethene, 60.6 mol percent. The melt index of product was about 0.58 grams/10 minutes.

EXAMPLE III.

Ethylene was polymerized in the same manner described in EXAMPLE I. The catalyst was 2.0 weight percent chromium trioxide on W. R. Grace No. 952 SiO₂. Catalyst was calcined at 1200°F. with dry oxygen for 12 hours. Catalyst, triisobutylaluminum and ethene were continuously charged to the reactor at 210°F. under 300 psig pressure. Hydrogen was charged as needed to maintain 35 mol percent H₂ in the reactor. The mole ratio of Al(i-Bu)₃/CrO₃ was 3. The polymer yield based on catalyst was 4,600 grams/gram. Polymer was removed continuously as a melt. The polymer produced showed the following physical properties:

TABLE III

| Cut | M.I. | MF ₁₀ | MF ₁₀ /MF ₁ | Wt. Percent Extractables | Wt. Percent Volatiles | \bar{M}_w/\bar{M}_n |
|-----|------|------------------|-----------------------------------|--------------------------|-----------------------|-----------------------|
| 5 | 0.20 | 22.2 | 111 | 1.5 | 0.65 | 14.7 |
| 6 | 0.12 | 16.6 | 138 | 1.6 | 0.87 | 17.0 |
| 7 | 0.12 | 20.2 | 168 | 1.8 | 0.98 | 15.4 |

EXAMPLE IV.

Propylene was polymerized by an active titanium chloride catalyst with diethylaluminum chloride cocatalyst continuously in the gas phase under conditions tabulated in

Table IV. The propene served as its own quench liquid for heat removal. Polymer was intermittently removed as particulate through a double ball-valved lock chamber attached to the take-off end of the reactor.

TABLE IV
POLYMERIZATION OF PROPYLENE

| | | | | | | | |
|---|--------------------|--------------------------------|------------------|--------------------------------------|------------------|--|--|
| | | Catalyst: Titanium trichloride | | Cocatalyst: Diethylaluminum chloride | | Conditions: 160°F, 300 psig, 1 mole percent hydrogen | |
| Time on stream, minutes | 145 | 270 | 153 | 225 | 162 | | |
| Type of catalyst addition | Batch | Batch | Continuous | Batch | Continuous | | |
| Et ₂ /AlCl ₃ /TiCl ₄ ratio | 2.8 | 2.8 | 3.0 | 2.8 | 2.9 | | |
| TiCl ₃ addition rate, milligrams/hour | 48 ⁽¹⁾ | 24-48 ⁽²⁾ | 45 | 24-48 ⁽²⁾ | 46 | | |
| Total polymer produced, grams | 165 | 486 | 296 | 358 | 300 | | |
| Polymer yield, grams/gram | (0-145 min) 1970 | (0-270 min) 3120 | (0-153 min) 2600 | (0-225 min) 2980 | (0-162 min) 2040 | | |
| | (0-60 min) 640 | (0-60 min) 1225 | | (0-90 min) 172 | | | |
| | (60-145 min) 4600 | (60-120 min) 3800 | | (90-225 min) 7200 | | | |
| | | (120-180 min) 5300 | | | | | |
| | | (180-240 min) 4700 | | | | | |
| | | (240-270 min) 3000 | | | | | |

⁽¹⁾ A 12 milligram portion of catalyst added every 15 minutes up to 90 minutes. No catalyst added after 90 minutes.

⁽²⁾ A 12 milligram portion of catalyst added every 15 minutes up to 90 minutes. A 12 milligram portion of catalyst added every 30 minutes from 90 to 270 minutes.

EXAMPLE V.

A supported titanium chloride catalyst and triethylaluminum catalyst were employed in the same manner as described in Example I using approximately 3 fol percent propylene in the reactor gas to copolymerize with the ethylene. Liquid propylene was added continuously at the rate of 30 milliliters/hour which maintained its concentration at 3 mol percent in the reactor gas. Copolymer was re-

moved by way of a double ball-valved lock chamber attached to the take-off end of the reactor as particulate. Catalyst and cocatalyst were deactivated by treating the copolymer with 250°F. steam. A copolymer inhibitor package was added and the product thereof was melt extruded in the normal manner to form product pellets. Conditions of two such runs are shown in Table V below.

5

10

15

20

TABLE V

| Run period | 1 | 2 | 3 | 4 | 5A | 5B | 6 | 7 | 8 | 9 | 10 | 11 |
|--|------|------|------|----------|------|------|------|------|------|--------|------|------|
| Time on stream, hours, minutes | 5,12 | 3 | 5,20 | 4,22 | 3,8 | 3,8 | 6,37 | 7,10 | 6,55 | 4,22 | 3,15 | 2,45 |
| Temperature, °F. | 179 | 178 | 179 | 177 | 178 | 178 | 180 | 182 | 186 | 185 | 207 | 207 |
| Total pressure, psig | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| Ave. catalyst, feedrate, milligrams/hour | 37.0 | 29.1 | 30.9 | 33.3 | 40.2 | 40.2 | 42 | 37 | 33.3 | 37.9 | 39.2 | 41.0 |
| *TEA/CAT | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 15 | 7.5 | 7.5 | 7.5 | 15 | 15 | 7.5 |
| Recycle gas composition mol percent | | | | | | | | | | | | |
| Hydrogen | 38 | 35 | 36 | 31 | 40 | 40 | 42 | 41 | 39 | 36 | 36 | 36 |
| Ethylene | 52 | 44 | 52 | 61 | 48 | 48 | 41 | 46 | 50 | 55 | 52 | 52 |
| Ethane | 6.6 | 20.5 | 7.8 | 4.2 | 8.6 | 8.6 | 12.6 | 8.8 | 7.0 | 5.1 | 8.3 | 8.3 |
| Propylene | 2.3 | 3.2 | 3.2 | 3.2 | 2.6 | 2.6 | 3.1 | 2.9 | 3.4 | 2.9 | 3.2 | 3.2 |
| Isopentane | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Reactor bleedrate, cubic feet/hour | 0.87 | 0.86 | 0.59 | 0.61 | 0.69 | 0.69 | 0.63 | 0.64 | 0.63 | 0.62 | 0.59 | 0.59 |
| Polymer produced, grams | 500 | 690 | 822 | 1357 | 0 | 165 | 339 | 1416 | 1015 | 1764 | 754 | 348 |
| Catalyst yield, gram/grams | 2600 | 8000 | 4980 | 9320 | 0 | 620 | 1150 | 5345 | 4410 | 10,660 | 5915 | 3130 |
| Melt index, gram/10 minutes | 0.17 | 0.2 | 0.2 | 0.17-1.0 | - | - | - | 6-7 | 6-7 | 6-7 | 6-7 | 6-7 |

TABLE V (Cont'd.)

| Run period | 1 | 2 |
|---|-----------|-----------|
| Time on stream, hours, minutes | 4,53 | 5,15 |
| Temperature, °F. | 193 | 200 |
| Total pressure, psig | 300 | 300 |
| Ave. cat. feedrate, milligrams/hour TEA/CAT* | 40 7.5 | 28 7.5 |
| Recycle gas comp., mol percent | | |
| Hydrogen | 44 | 42 |
| Ethylene | 45 | 46 |
| Ethane | 7.0 | 8.0 |
| Propylene | 2.9 | 2.95 |
| Isopentane | 1 | 1 |
| Reactor bleedrate, cubic feet/hour | 0.62 | 0.67 |
| Polymer produced, grams | 1055 | 1539 |
| Catalyst yield, grams/grams | 5375 | 8800 |
| Melt index, grams/10 minutes | 12-20 | 17-19 |

*TEA/CAT is the weight ratio of triethylaluminum to catalyst used.

EXAMPLE VI.
A supported titanium chloride catalyst and triethylaluminum cocatalyst were employed for the polymerization of ethene in the same manner as Example I. Polymer was removed by way of a double ball-valved lock chamber as particulate. Catalyst was deactivated by treating with steam at 250°F. Polymer inhibitor package was added and the result thereof was melt extruded in the normal manner to form product pellets. Polymerization product conditions and properties of some of the various cuts are shown below in Tables VI and VII.

TABLE VI

| Polymerization Conditions | | | | | | | | | | | | | |
|--|-------|---------|---------|---------|---------|--------|------|-------|--------|---------|-------|--------|--------|
| Temperature, Section 1 °F | 180 | 160-205 | 160-205 | 160-205 | 160-205 | 205 | 190 | 195 | 195 | 185 | 190 | 190 | 190 |
| Temperature, Section 2 °F | 175 | 160-205 | 160-205 | 160-205 | 160-205 | 205 | 189 | 192 | 190 | 182 | 186 | 190 | 190 |
| Exit port °F | 165 | 170 | 170 | 170 | 170 | 170 | 173 | 175 | 172 | 170 | 174 | 170 | 170 |
| Solvent reservoir | 137 | 150 | 150 | 145 | 150 | 150 | 152 | 152 | 152 | 152 | 156 | 140 | 140 |
| Pressure, psig | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| Reaction gas composition, mol % | | | | | | | | | | | | | |
| Hydrogen | 25 | 22 | 22 | 20 | 25 | 25 | 60 | 35 | 42 | 40 | 44 | 55 | 55 |
| Ethylene | 74 | 77 | 77 | 79 | 73 | 72 | 39 | 64 | 56 | 59 | 55 | 41 | 41 |
| Ethane | 0.2 | 0.3 | 0.3 | 0.2 | 0.4 | 0.9 | 0.3 | 0.6 | 0.6 | 0.4 | 3.0 | 0.4 | 0.4 |
| Isopentane | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Reactor vent rate, cubic feet/hour | 0.67 | 0.67 | 0.67 | 1.92 | 1.05 | 0.20 | 0.65 | 0.72 | 0.77 | 0.75 | 0.80 | 0.72 | 0.72 |
| Catalyst | | | | | | | | | | | | | |
| Feeder conc. milligrams/liter | 125 | 125 | 62.5 | 62.5 | 62.5 | 62.5 | 62.5 | 125 | 80 | 62.5 | 31.2 | 40 | 40 |
| Feed rate, milligrams/hour | 31.9 | 25.2 | 10.6 | 8.7 | 11.9 | 4.85 | 21.8 | 17.2 | 9.1 | 2.9 | 11.6 | 11.0 | 11.0 |
| Cocatalyst | | | | | | | | | | | | | |
| AlEt ₃ feeder conc., milligrams/liter | 1,250 | 1,250 | 625 | 625 | 625 | 625 | 625 | 1,250 | 800 | 625 | 313 | 200 | 200 |
| AlEt ₃ feed rate, milligrams/hour | 319 | 252 | 106 | 87 | 119 | 485 | 218 | 172 | 91 | 29 | 116 | 55 | 55 |
| Weight ratio AlEt ₃ /catalyst | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 7.5 | 5 | 5 |
| Polymerization Results | | | | | | | | | | | | | |
| Total run time, hours | 9.8 | 14.8 | 1.8 | 6.2 | 7.5 | 7.8 | 20.9 | 7.5 | 2.5 | 5.8 | 6.5 | 22.9 | 22.9 |
| Total polymer produced, grams | 663 | 2,107 | 781 | 619 | 1,146 | 749 | 52 | 366 | 429 | 3,335 | 2.05 | 3,077 | 3,077 |
| Polymer yield on catalyst, grams/gram | 2,000 | 5,660 | 41,700 | 11,600 | 12,800 | 19,700 | — | 2,830 | 19,240 | 204,000 | 2,715 | 12,200 | 12,200 |

TABLE VII

| | Cuts 13-22 | Cuts 23-39 |
|---|------------|------------|
| <u>General Properties</u> | | |
| Annealed density, g/cc | 0.9734 | 0.9787 |
| Inherent viscosity, dl/g | 1.99 | 1.28 |
| Melt index, MF_1 , g/10 min | 1.1 | 7.3 |
| Melt index, MF_{10} , g/10 min | 35 | 234 |
| Flow rate ratio, MF_{10}/MF_1 | 32 | 32 |
| Hexane extractables, wt % | 0.30 | 0.70 |
| Oven volatiles content, wt. % | 0.04 | 0.33 |
| Stiffness, psig | 137,000 | 179,000 |
| <u>Tensile Properties</u> | | |
| Tensile strength at yield, psig at 2 in/min. | 4,520 | — |
| Tensile strength at ultimate, psig at 2 in/min | 2,940 | 4,850 |
| Elongation at yield, % at 2 in/min | 11 | — |
| Elongation at ultimate, % at 2 in/min | 1,100 | 9.9 |
| <u>Impact Properties</u> | | |
| Tensile Impact strength, ft-lb/in ² | 82 | 22 |
| Izod impact strength, ft-lb/in ² | 9.7 | 0.55 |
| <u>Thermal Properties</u> | | |
| Vicat Softening point, °F | 263 | 259 |

EXAMPLE VII.

Propylene was polymerized in essentially the same manner described in EXAMPLE I. The recycle gas and quench liquid were propylene. The melter temperature was 350°F. while the catalyst kill section operated at 400°F. An active titanium chloride catalyst (33 milligrams) with diethylaluminum chloride cocatalyst (77 milligrams), mol ratio Al/Ti = 3, was charged to the reactor every thirty minutes. Hydrogen was added as needed to maintain 2.9 mol percent in the reactor gas cap. The reactor temperature was maintained at 160°F. and the reactor pressure was controlled at 300 psig by controlling temperature in the recycle condenser at about 120°F. A polymer yield based on catalyst of 10,000 grams/gram was obtained. The polymer was removed from the reactor as a melt. The polymer showed a melt flow rate of 16.4 grams/10 minutes at 230°C. under a load of 2,060 g. The 68°C. n-hexane extractables was 4.0 weight percent.

EXAMPLE VIII.

Ethylene was polymerized in the same manner described in EXAMPLE I except in this case two sections of the reactor were maintained at different temperatures. Reactor section one was operated at 160°F. while reactor section two was operated at 210 to 230°F. This was accomplished by varying the amount

of isopentane quench added to each section. The catalyst used was a supported titanium compound and an aluminum triethyl cocatalyst was added in a weight ratio of cocatalyst to catalyst of three to one. The reactor pressure was controlled at 300 psig. and the hydrogen concentration was maintained at 40 mol percent. A polymer yield of 62,000 grams of polymer/gram of catalyst was obtained. The polymer melt index was measured at 5.5 with a MF_{10}/MF_1 of about 40 and a spiral flow of 18 inches. Polymer having the same M.I. made under single temperature conditions showed an MF_{10}/MF_1 value of about 34 and demonstrated a spiral flow of about 16 inches.

Spiral flow is an empirical method of assessing ease of processability of a polymer by measuring the length of flow in a special mold under specific temperature and pressure conditions. The longer the spiral flow the easier is the processability.

The following examples illustrate the invention using the reactor divided into two compartments.

EXAMPLES IX—XI.

A carbon steel reactor approximately two feet in diameter by 3.0 feet in length and divided into two polymerization zones was used for the polymerization of ethene. Quench liquid was isopentane. Catalyst was a titanium

compound supported on a magnesium compound supported on a magnesium compound and cocatalyst was triethylaluminum added in a weight ratio, cocatalyst/catalyst, of about six and at a catalyst rate of about 0.2 gram per hour. Production rate was about twelve pounds per hour. Catalyst and cocatalyst were added separately to the first polymerization zone and product was removed from the second polymerization zone of the reactor, the zones being separated by a divider as described above.

Melt indices and inherent viscosities were measured by ASTM tests D 1238-72 (Cond. E) and D 2857 respectively. The ratio of weight average molecular weight to number average molecular weight, $\overline{M}_w/\overline{M}_n$, was measured by gel permeation chromatography.

Examples IX, X and XI as shown in Table VIII illustrate the effect upon molecular weight of operating two polymerization zones at two different hydrogen levels as compared to operation of the two zones of the reactor at a single hydrogen level. Example IX represents a product produced from single hydrogen operation at a total pressure of 400 psig in which the polymerization is carried out at 210°F with 25 mol percent hydrogen in the recycle gas. The product has an inherent viscosity (η), of 2.0 dl/gram, a melt index of 0.97 grams/10 minutes and a relatively narrow molecular weight distribution, $\overline{M}_w/\overline{M}_n=6$. Similarly, when the reactor is run at 210°F and 57 mol percent hydrogen, product properties are ($\eta=1.02$ dl/gram, M.I.=28.6 and $\overline{M}_w/\overline{M}_n=6$. When the reactor is run at 210°F and 5 mol percent hydrogen, product

properties are (η)=4.5 dl/gram. At the latter high molecular weight accurate melt index measurements are difficult and were not made.

In Example X of Table VIII the results given are for a polymerization in which the first polymerisation zone of the reactor was held at about 210°F/26 mol percent hydrogen and the second polymerization zone was held at about 210°F/12 mol percent hydrogen and the relative production of polymer made in the first and second zones was in a 42/58 weight ratio. The product exiting from the reactor had an inherent viscosity of 2.1 dl/gram and a melt index of 0.68. However, the measured $\overline{M}_w/\overline{M}_n$ of the product had increased to about 9 which improved the rheological properties.

Example XI in Table VIII shows the results of a polymerization in which the first polymerization zone of the reactor was operated at 210°F/57 mol percent hydrogen and the second polymerization zone was operated at 210°F/5 mol percent hydrogen. By controlling the relative proportions of materials made in the first and second zones to a 70/30 ratio, the product exiting the reactor had an inherent viscosity of 1.99 dl/gram and a melt index of 0.67 grams/10 minutes. However, the measured $\overline{M}_w/\overline{M}_n$ of the product had increased to about 12. The changes in rheological properties by dual hydrogen operation are shown by the decrease in apparent viscosity at 5 sec^{-1} , 5.5 vs. 5.2×10^4 poise, the increase in shear rate for the beginning of oscillating flow, 650 vs 1560 sec^{-1} , and the increase in shear rate for melt fracture [$\gamma(\text{MF})$], 2400 vs 6900 sec^{-1} .

TABLE VIII

| Example Number | Components | | | | Split First/Second Zone | Product | | Rhenology | | | |
|----------------|------------|------|----------|------|-------------------------|------------------------|-----------------|---------------------------------|---|---------------------------|---------------------------|
| | 1 | | 2 | | | $(\eta, \text{dl/gm})$ | M.I. (g/10 min) | $(\frac{\bar{M}_w}{\bar{M}_n})$ | App. visc. at 5 sec ⁻¹ ($\times 10^{-4}$ poise) | SROF (sec ⁻¹) | (MF) (sec ⁻¹) |
| | (η) | M.I. | (η) | M.I. | | | | | | | |
| | | | | | | | | | | | |
| IX | 2.0 | 0.97 | — | — | 100/0 | 2.0 | 0.97 | 5.6 | 5.5 | 650—2100 | 2400 |
| X | 1.02 | 28.6 | 2.83 | 0.16 | 42/58 | 2.10 | 0.68 | 9.1 | 5.6 | 928—1940 | 5100 |
| XI | 1.02 | 28.6 | 4.5 | * | 70/30 | 1.99 | 0.67 | 11.7 | 5.2 | 1560—2630 | 6900 |

* Too low to measure accurately.

WHAT WE CLAIM IS:—

1. A continuous process for vapor phase polymerization of at least one polymerizable monomer, which process comprises polymerizing said monomer in the vapor phase, in a horizontal polymerization zone and in the presence of catalyst and a stirred subfluidized (as defined herein) particulate polymer bed in said zone; spraying a readily vaporizable quench liquid onto the surface of said stirred particulate polymer bed to control the polymerization temperature by evaporative cooling in said polymerization zone; removing off-gases comprising monomer vapor and quench liquid vapor from said polymerization zone to form an off-gas stream; and recovering particulate polymer from said polymerization zone.

2. A process according to Claim 1 wherein said particulate polymer bed is divided into two or more temperature-controllable sections.

3. A process according to Claim 1 or Claim 2 wherein said off-gas stream is condensed to form a quench liquid recycle stream and a gaseous recycle stream comprising monomer vapor, and said streams are separately returned to said polymerization zone.

4. A process according to Claim 3 wherein a portion of said quench liquid recycle stream is returned to said polymerization zone with at least one catalyst component.

5. A process according to any preceding claim wherein said monomer is polymerized in two or more of said horizontal polymerization zones serially interconnected for transferring particulate polymer therebetween, and particulate polymer is recovered from the last of said zones.

6. A process according to any of Claims 1 to 5 wherein said monomer comprises ethene.

7. A process according to any of Claims 1 to 5 wherein said monomer comprises propene.

8. A process according to any of Claims 1 to 5 wherein said monomer comprises butene-1.

9. A process according to any of Claims 1 to 5 wherein said monomer comprises 4-methyl-pentene-1.

10. A process according to any of Claims 1 to 5 wherein said monomer comprises butadiene.

11. A process according to any of Claims

- 1 to 5 wherein said monomer comprises styrene.
12. A process according to any of Claims 1 to 5 wherein said monomer comprises vinyl chloride.
13. A process according to any preceding claim wherein said quench liquid comprises isobutane or isopentane.
14. A process according to Claim 7 in which said quench liquid comprises propene, a mixture of propene and isobutane or a mixture of propene and isopentane.
15. A process according to any preceding claim wherein said monomer is polymerized in the presence of hydrogen.
16. A continuous vapor phase polymerization process according to Claim 1 and substantially as hereinbefore described.
17. A continuous vapor phase polymerization process according to Claim 1 and substantially as described in any of the Examples.
18. Polymer whenever produced by a process according to any preceding claim.
19. A polymerization reactor for carrying out the polymerization process claimed in any preceding claim comprising a generally cylindrical reaction vessel arranged with its axis horizontal so as to provide at least one horizontal polymerization zone therein; a centrally located rotatable shaft extending longitudinally through the reactor to which are attached a plurality of adjacently located and circularly offset flat impellers; drive means for rotating said shaft; one or more inlets spaced along the bottomward part of the reactor for introducing feed-gas comprising monomer vapor to said polymerization zone; one or more inlets for introducing catalyst to said polymerization zone; one or more inlets spaced along the topward part of the reactor for introducing quench liquid to said polymerization zone; one or more outlets spaced along the topward part of the reactor for removing off-gases from said polymerization zone; and means for removing polymer product from the reactor.
20. A reactor according to Claim 19 wherein said polymerization zone contains at least one weir to form at least two temperature controllable polymerization sections therein.
21. A reactor according to Claim 19 or Claim 20 wherein the reactor vessel contains at least two polymerization zones, each zone being separated from the adjacent zone by a divider having an opening in the bottomward portion thereof for transfer of particulate polymer between said zones.
22. A reactor according to any one of Claims 19 to 21 wherein a take-off zone containing at least one impellor is formed by a divider at one end of the reactor, said divider containing an opening in the upper portion thereof to allow passage of gas and to control movement of particulate polymer in the direction towards said end of the reactor, said take-off zone containing an opening connected to said means for removing particulate polymer from the reactor.
23. A reactor according to Claim 19 and substantially as hereinbefore described.
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FIG. 1

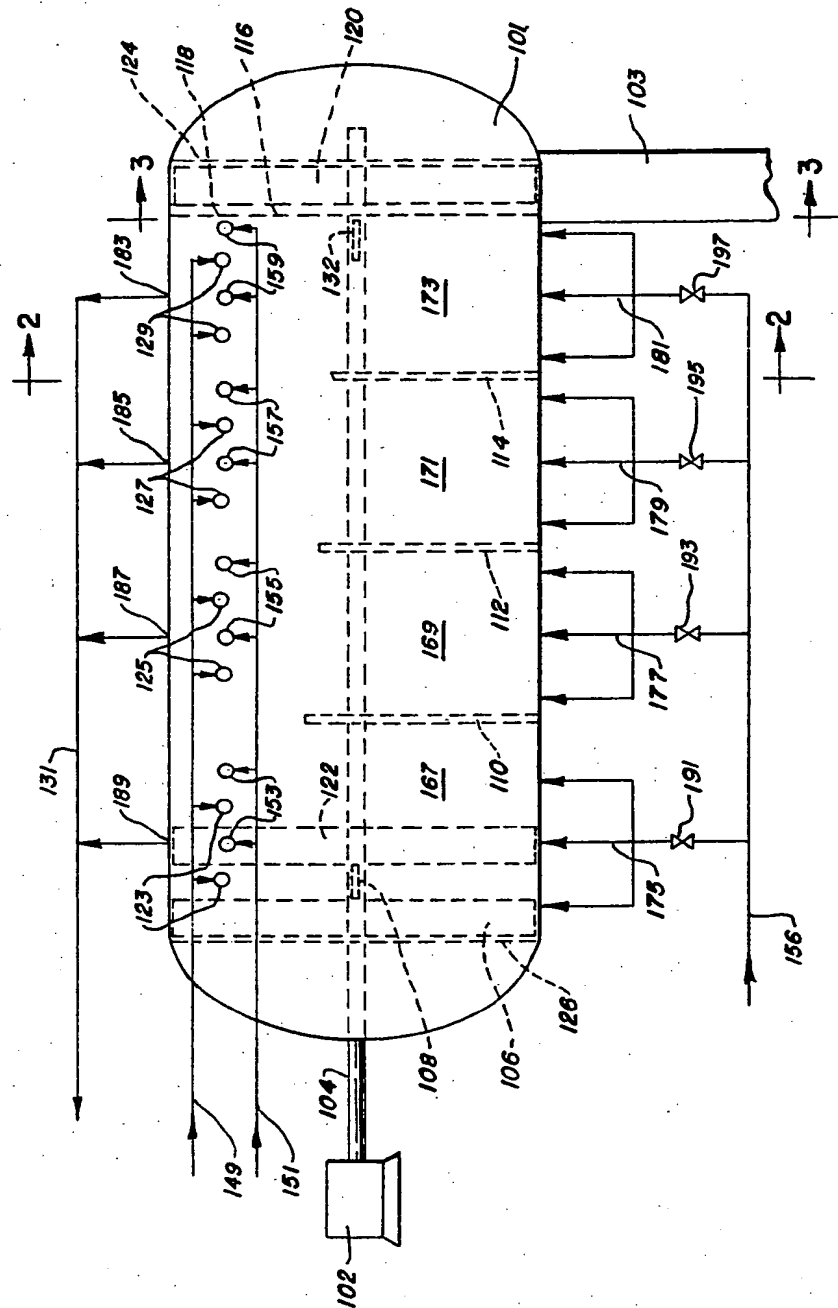


FIG. 2

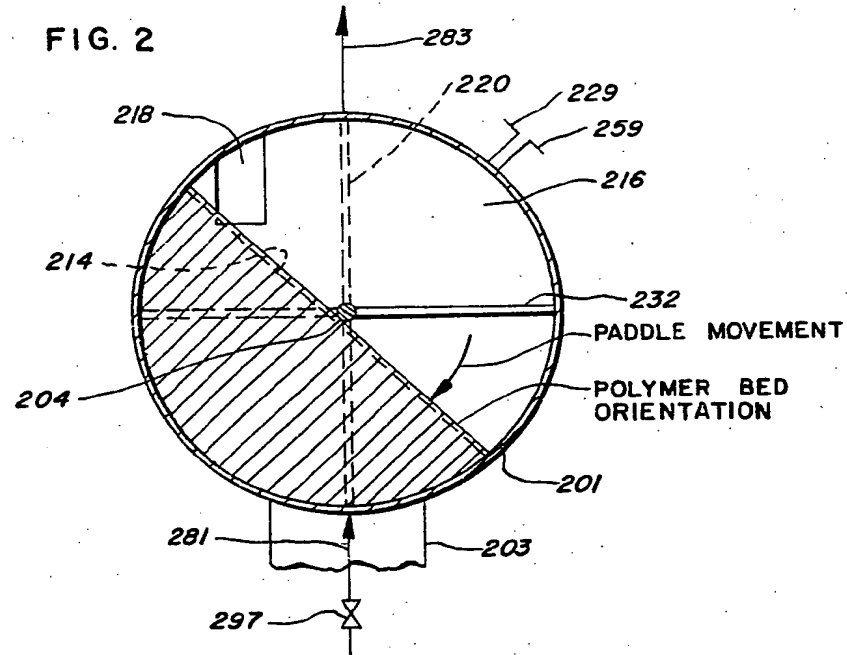
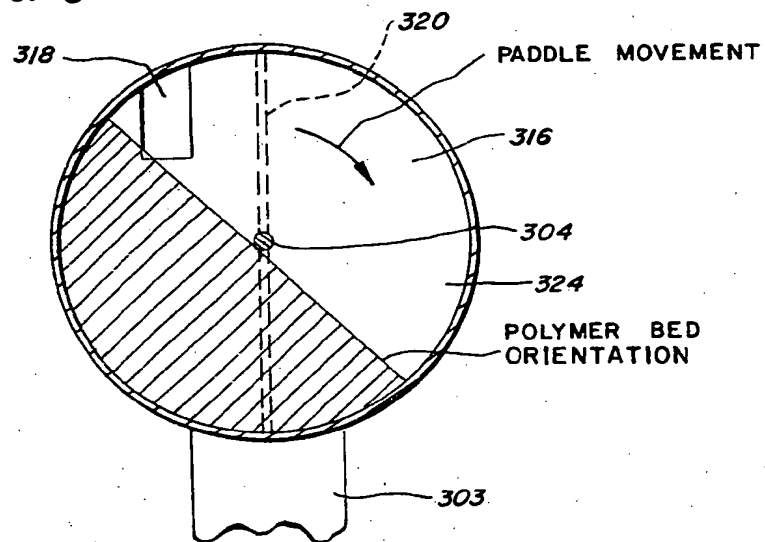


FIG. 3



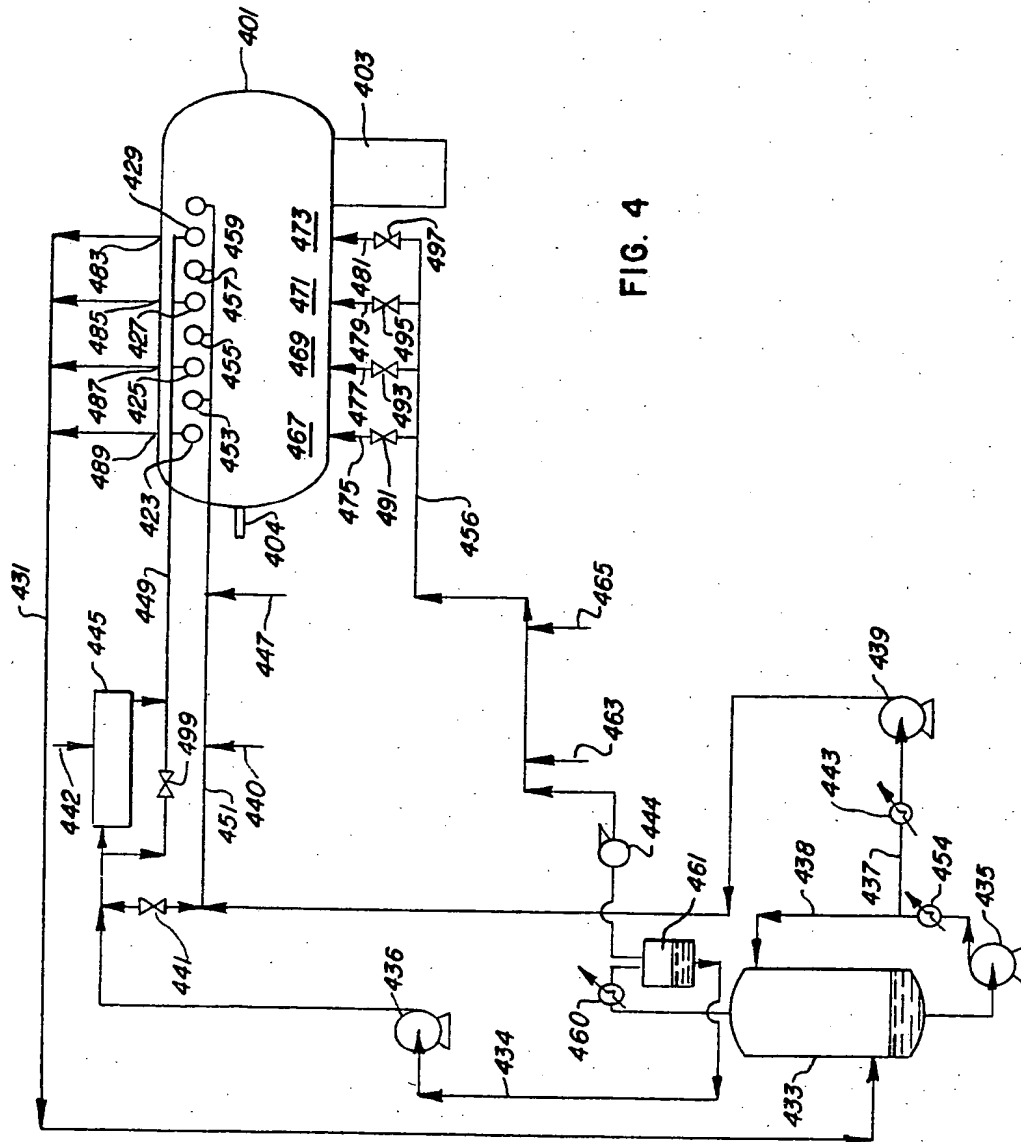
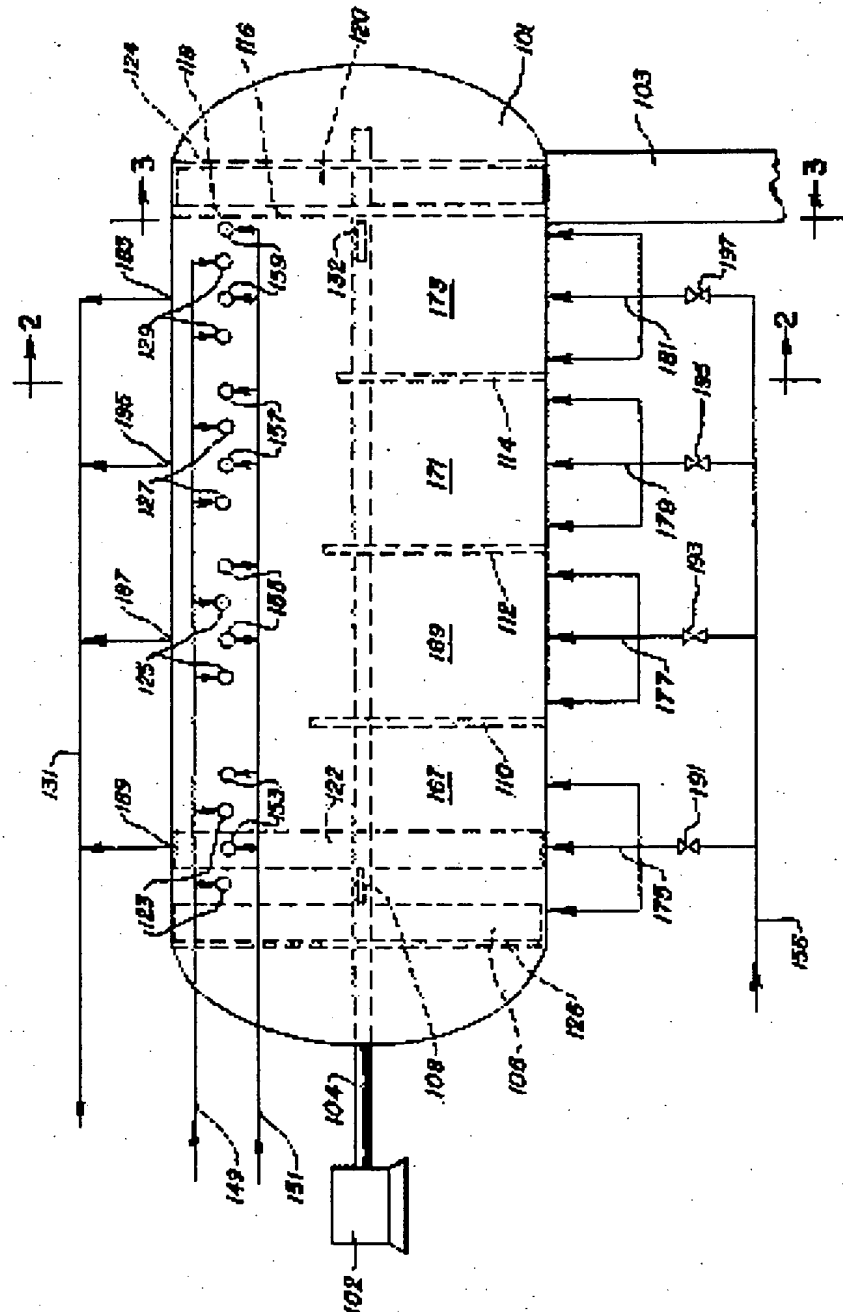
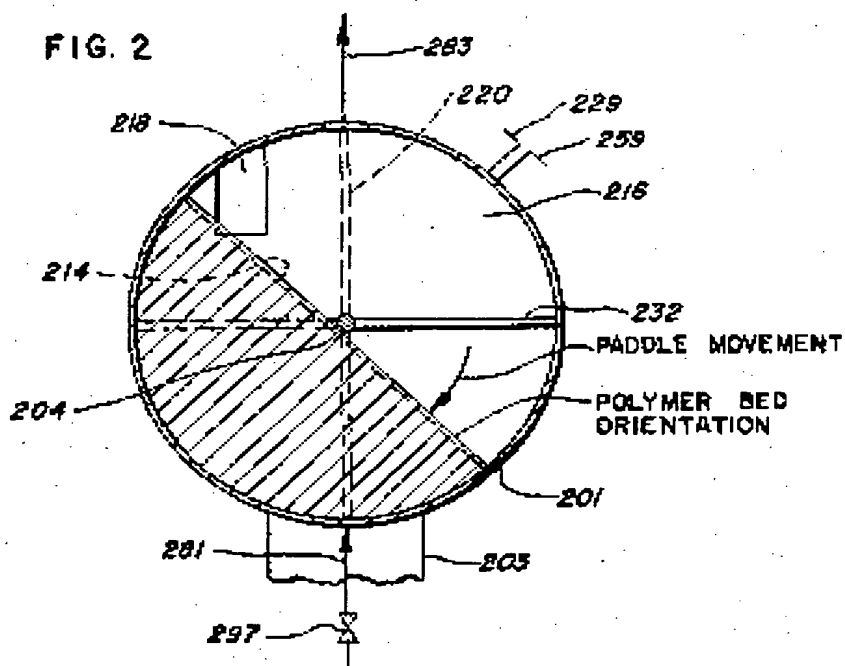
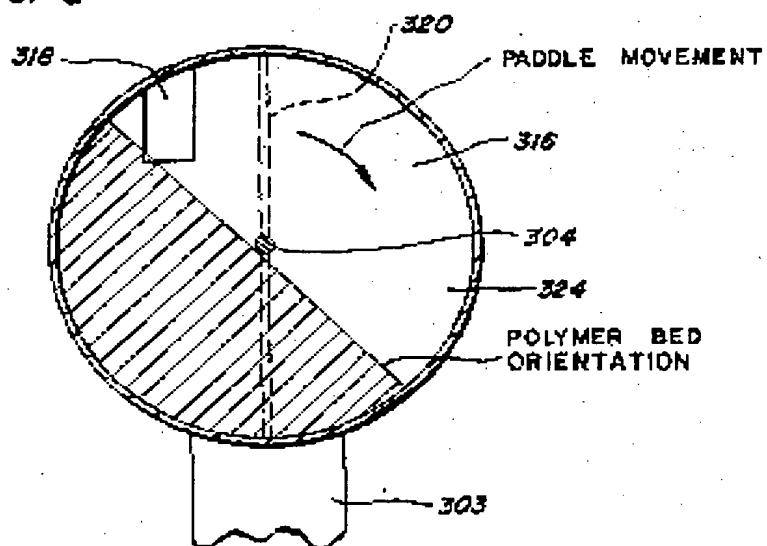
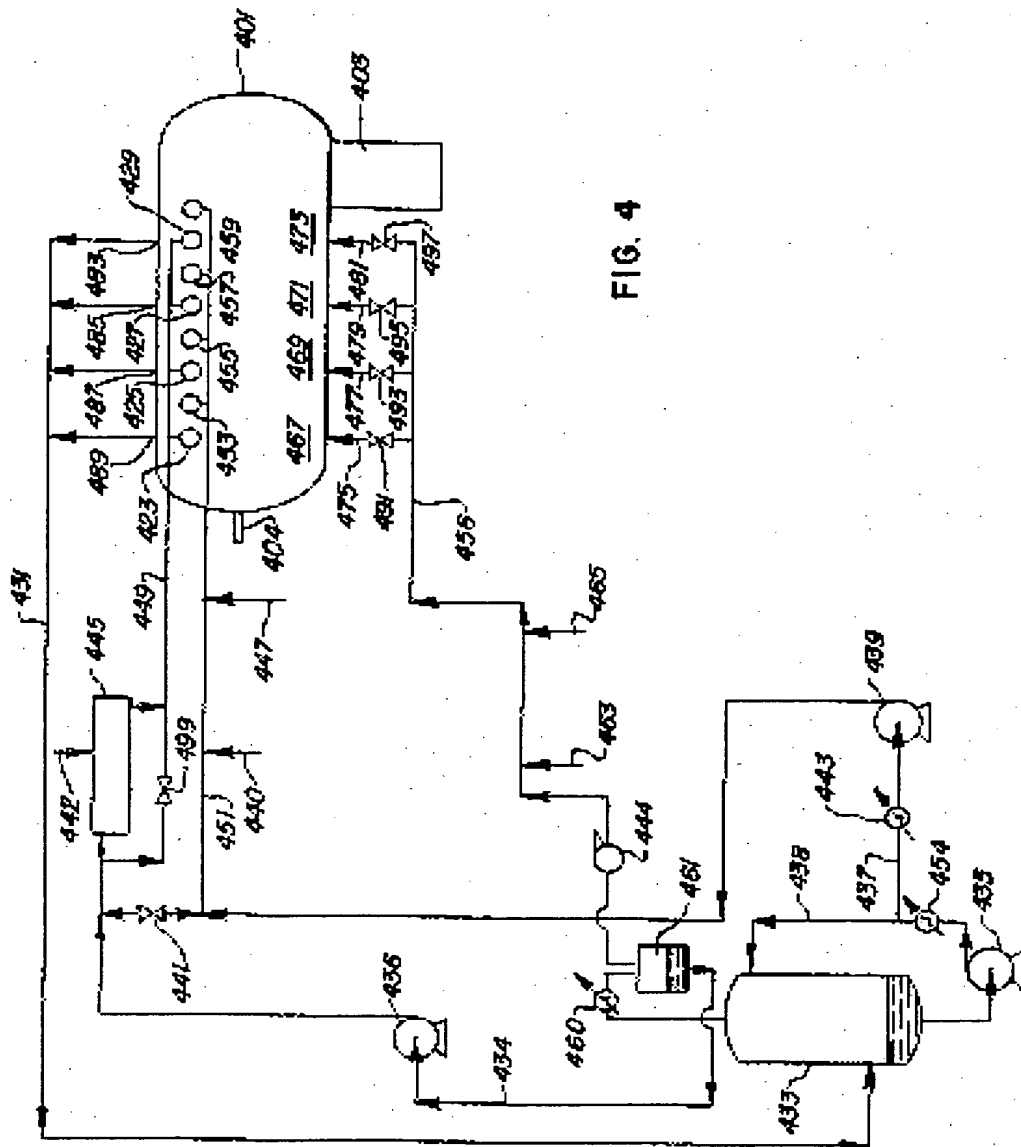


FIG. 4

FIG. 1



**FIG. 3**



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